DRAFT Rationale For Proposed Revisions To Ambient Water Quality Criteria For Ammonia



Prepared by:

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Appendix

Ammonia Chemistry and Example Calculations of Ammonia Aquatic Life Criteria

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Background

Under the Clean Water Act, EPA is required to publish and periodically update ambient water quality criteria. The latest scientific knowledge on the effects of water pollutants on public health and welfare, aquatic life, and recreation are reflected in these updates. The most up-to-date recommendations for developing freshwater aquatic life criteria for ammonia have been published by the U.S. Environmental Protection Agency (EPA) in "1999 Update of Ambient Water Quality Criteria for Ammonia" (1999 Ammonia Update). The document provides the rationale and the methodology used in formulating revised acute and chronic aquatic life ammonia water quality criteria that address the temperature- and pH-dependence of ammonia toxicity.

Aquatic life water quality toxicity criteria are generally expressed as acute or chronic values. Acute refers to the toxic effects in the short term (1 hour average) and acute symptoms include visible signs of stress, like disorientation and death. Chronic refers to toxicity in the long term (30 day average); the chronic effects being not as visible and much more subtle. These effects may include poor life cycle success, decreased reproduction, kidney dysfunction, and gill tissue damage.

EPA initially published ammonia aquatic life criteria in 1984. The procedures used to develop the 1984 criteria resulted in determination of single-value criteria expressed as un-ionized ammonia. The recommended 1984 ammonia aquatic life criteria were 0.02 mg/L NH₃ for coldwater fish and 0.06 mg/L NH₃ for warmwater fish.

Revisions were made to the 1984 criteria based on subsequent ammonia toxicity research results and recalculation of ammonia aquatic life criteria. Revised freshwater criteria for ammonia were published in 1992, 1996, and 1998. The procedures used in these revisions resulted in "calculated" un-ionized ammonia criteria which varied depending on the pH and temperature of the waterbody.

The 1999 Update contains EPA's most recent recommended freshwater aquatic life criteria for total ammonia and supersedes all previous freshwater aquatic life ammonia criteria. The new proposed criteria reflect recent research and data since 1984, and are a revision of several of the procedures used to determine the 1984 criteria. As a result of these revisions, the recommended 1999 criteria are not

single-values but instead are site-specific values determined via algebraic relationships. The acute criteria for ammonia are dependent on pH and whether sensitive coldwater fish species are present. Chronic criteria are recommended based on the pH and temperature of the water body and are categorized depending on whether fish early life stages are present or absent. In previous criteria recommended by EPA, when chronic toxicity data was lacking, an acute-chronic ratio relationship was used to estimate a chronic criteria from an acute value. In the 1999 Update, the acute-chronic ratio relationship is no longer used, and both the acute and chronic criteria are expressed in terms of total ammonia nitrogen rather than un-ionized ammonia as had been the convention used in prior ammonia criteria recommendations.

Overview

Ammonia is a colorless, gaseous, alkaline compound of nitrogen and hydrogen that is highly soluble in water. It is a biologically active compound present in most waters as a normal biological degradation product of nitrogen organic matter. Ammonia can also reach groundwater and surface waters from the discharge of industrial operations that use ammonia or ammonia salts.

In natural water, ammonia exists in two forms: un-ionized ammonia (NH₃) and ammonium (NH₄⁺). The term total ammonia refers to the sum of the two forms (NH₃ and NH₄⁺). Undissociated ammonia (NH₃) has been recognized as the more toxic form. The toxicity of ammonia to fish is due to the diffusion and buildup of ammonia in the gill tissue and the blood stream.

The amounts or concentrations of the individual ammonia species (forms) that are present in aqueous solutions are dependent on various physiochemical properties of the solution, in particular, temperature, pH, and ionic composition. In fresh water, the effect of ionic composition on ammonia speciation is much smaller than the effects of pH and temperature. Due to this small effect, the ionic strength of the solution is generally not considered as a significant variable affecting ammonia toxicity in freshwater systems.

An overview of the chemical relationships and equilibrium equations governing the ammonia-water system is presented in the Appendix section of this document.

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1999 Ammonia Criteria

In developing the 1999 Ammonia Criteria, EPA reviewed and analyzed previous ammonia toxicity data as well as recent toxicity data and results. Although the past convention had been to express ammonia toxicity as un-ionized ammonia, considered the more toxic ammonia form, EPA reanalyzed the freshwater toxicity data in terms of total ammonia. The rationale behind this was since permit limits, compliance schedules, and sample analyses are usually expressed in terms of total ammonia, implementation of a total ammonia water quality criteria would eliminate having to convert total ammonia concentrations to un-ionized ammonia values.

Acute Criteria

In re-examing the ammonia toxicity data, EPA found no consistent trend or relationship with temperature when acute toxicity was expressed as total ammonia. On the basis of this analysis, the 1999 Ammonia Update does not include any temperature dependent variable in the formulas for calculating acute ammonia toxicity criteria. Rather, the acute ammonia criteria are dependent on whether salmonids and other sensitive coldwater fish species are present or absent, and are expressed as a function of solution pH. Salmonids refer to the family of fishes that are dominant in the coldwater streams and lakes of North America, and include salmon and trout, whitefishes, and graylings.

The following equations are presented in the 1999 Ammonia Update for deriving fresh water ammonia acute criteria (CMC - criteria maximum concentration).

When coldwater fish are present:

$$CMC = \frac{0.275}{(1+10^{7.204-pH})} + \frac{39.0}{(1+10^{pH-7.204})}$$

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When coldwater fish are not present:

$$CMC = \frac{0.411}{(1+10^{7.204-pH})} + \frac{58.4}{(1+10^{pH-7.204})}$$

A summary of the 1999 ammonia acute criteria values over the pH range 6.5 to 9.0 for the presence or absence of coldwater fish species is shown in Table 1 and graphically displayed in Figure 1. As noted in Table 1, the one-hour average concentration of total ammonia may not be exceeded more than once every three years on the average. The calculated acute criteria are more restrictive at higher pH values and when coldwater fish species are expected to be present.

Chronic Criteria

EPA reviewed and analyzed all of the chronic toxicity data used in the 1984 criteria document as well as available newer chronic toxicity data. The data was assessed and evaluated in terms of survival, growth, and/or reproduction of aquatic life. This permitted development of applicable formulas that could be used to calculate total ammonia chronic continuous criteria (CCC) values rather than using acute-chronic ratios to develop ammonia chronic concentrations as had been done to develop the previous chronic criteria. The endpoints selected by EPA for differentiating the 1999 chronic criteria were the presence or absence of fish early life stages, rather than the presence of coldwater or warmwater fish. The ammonia chronic criteria presented in the 1999 Ammonia Update are temperature and pH-dependent values that are applied depending on whether early life stages of fish are present or absent. The chronic criteria (CCC - criteria continuous concentration) are calculated using the following equations

When fish early life stages are present:

$$CCC = \left[\frac{0.0577}{(1+10^{7.688-pH})} + \frac{2.487}{(1+10^{pH-7.688})}\right] \times MIN \left[2.85, 1.45 \times 10^{0.028 \times (25-T)}\right]$$

where $T = {}^{\circ}C$

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Table 1. The one-hour average (Acute Criteria) concentration for Total Ammonia (in mg nitrogen per liter) for the protection of fresh water aquatic life. (The concentration of total ammonia may not exceed the acute criterion listed under "Salmonids Present" and/or "Salmonids Absent", more than once every three years on the average.)

HOOTE	AMMONIA WATER QUA FRESHWATER AQUA								
(mg Nitrogen/L)									
pН	Salmonids Present ¹ (Coldwater Fish)	Salmonids Absent ² (Warmwater Fish)							
6.5	32.6	48.8							
6.6	31.3	46.8							
6.7	29.8	44.6							
6.8	28.1	42.0							
6.9	26.2	39.1							
7.0	24.1	36.1							
7.1	22.0	32.8							
7.2	19.7	29.5							
7.3	17.5	26.2							
7.4	15.4	23.0							
7.5	13.3	19.9							
7.6	11.4	17.0							
7.7	9.65	14.4							
7.8	8.11	12.1							
7.9	6.77	10.1							
8.0	5.62	8.40							
8.1	4.64	6.95							
8.2	3.83	5.72							
8.3	3.15	4.71							
8.4	2.59	3.88							
8.5	2.14	3.20							
8.6	1.77	2.65							
8.7	1.47	2.20							
8.8	1.23	1.84							
8.9	1.04	1.56							

¹ The acute water quality criteria for total ammonia where salmonids may be present were calculated using the following equation, which may also be used to calculate unlisted values:

Acute water quality criteria for ammonia (salmonids present) =

$$\left[\frac{0.275}{1+10^{7.204-pH}}\right] + \left[\frac{39.0}{1+10^{pH-7.204}}\right]$$

Acute water quality criteria for ammonia (salmonids absent) =

$$\left[\frac{0.411}{1+10^{7.204-pH}}\right] + \left[\frac{58.4}{1+10^{pH-7.204}}\right]$$

NOTES:

pH and temperature are field measurements taken at the same time and location as the water sample destined for the laboratory analysis of ammonia. If field measured pH and/or temperature values fall between the above tabular values, round field measured values according to standard rounding procedures to nearest tabular value to determine ammonia standard or use above described equations.

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² The acute water quality criteria for total ammonia where salmonids are absent were calculated using the following equation, which may also be used to calculate unlisted values:

When fish early life stages are absent:

$$CCC = \left[\frac{0.0577}{(1+10^{7.688-pH})} + \frac{2.487}{(1+10^{pH-7.688})}\right] \times 1.45 \times \left[10^{0.028 \times (25-MAX(T,7))}\right]$$

where
$$T = {}^{\circ}C$$

Separate chronic criteria applicable to cold water and warm water fish species are not proposed in the 1999 Ammonia Update. Summaries of the 1999 total ammonia fresh water chronic criteria are presented in Tables 2 and 3. As noted in tables, the chronic criteria are expressed as a thirty-day average and may not be exceeded more than once every three years on the average. Additionally, the highest 4-day average within the 30-day period should not exceed 2.5 times the chronic criteria. Graphical representations of the chronic criteria as a function of water pH and temperature are shown in Figures 2 and 3. Criteria concentrations for the pH range 6.5 to 9.0 and the temperature range 0 ° C to 30 ° C are provided in the tables and figures.

Examples of the calculation of total ammonia acute and chronic criteria using the 1999 Update equations are shown in the attached Appendix. These examples also illustrate how to interpret the empirical temperature relationships of the above chronic criteria equations.

A review of the new proposed ammonia aquatic life criteria (Tables 1 to 3) shows the following generalizations:

- the acute criteria are more restrictive for the presence of coldwater fish and the criteria become more restrictive as the solution pH increases,
- at temperatures below 15 ° C, the chronic criteria values are more stringent when early life stages of fish are expected to be present,
- at temperatures above 15 ° C, similar chronic criteria values are calculated for when fish early life stages are present and when fish early life stages are absent,
- at lower temperature values (14.5 ° C for fish early life stages present and 7 ° C for fish

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Table 2. The thirty-day average (Chronic Criteria) concentration for Total Ammonia (in mg nitrogen per liter) for the protection of fresh water aquatic life when fish early life stages may be present. (The concentration of total ammonia may not exceed the chronic more than once every three years on the average. In addition, the highest 4-day average within the 30-day period should not exceed 2.5 times the chronic criterion.)

	TABLE 2. CHRONIC AMMONIA CRITERIA FOR WATERS WHERE FRESHWATER FISH EARLY LIFE STAGES MAY BE PRESENT										
		WHERE	FRESHWA				MAY BE I	PRESENT			
	(mg Nitrogen/L) ¹ Temperature (°C)										
рН	0	14	16	18	20	22	24	26	28	30	
6.5	6.67	6.67	6.06	5.33	4.68	4.12	3.62	3.18	2.80	2.46	
6.6	6.57	6.57	5.97	5.25	4.61	4.05	3.56	3.13	2.75	2.42	
6.7	6.44	6.44	5.86	5.15	4.52	3.98	3.50	3.07	2.70	2.37	
6.8	6.29	6.29	5.72	5.03	4.42	3.89	3.42	3.00	2.64	2.32	
6.9	6.12	6.12	5.56	4.89	4.30	3.78	3.32	2.92	2.57	2.25	
7.0	5.91	5.91	5.37	4.72	4.15	3.65	3.21	2.82	2.48	2.18	
7.1	5.67	5.67	5.15	4.53	3.98	3.50	3.08	2.70	2.38	2.09	
7.2	5.39	5.39	4.90	4.31	3.78	3.33	2.92	2.57	2.26	1.99	
7.3	5.08	5.08	4.61	4.06	3.57	3.13	2.76	2.42	2.13	1.87	
7.4	4.73	4.73	4.30	3.78	3.32	2.92	2.57	2.26	1.98	1.74	
7.5	4.36	4.36	3.97	3.49	3.06	2.69	2.37	2.08	1.83	1.61	
7.6	3.98	3.98	3.61	3.18	2.79	2.45	2.16	1.90	1.67	1.47	
7.7	3.58	3.58	3.25	2.86	2.51	2.21	1.94	1.71	1.50	1.32	
7.8	3.18	3.18	2.89	2.54	2.23	1.96	1.73	1.52	1.33	1.17	
7.9	2.8	2.80	2.54	2.24	1.96	1.73	1.52	1.33	1.17	1.03	
8.0	2.43	2.43	2.21	1.94	1.71	1.50	1.32	1.16	1.02	0.897	
8.1	2.10	2.10	1.91	1.68	1.47	1.29	1.14	1.00	0.879	0.773	
8.2	1.79	1.79	1.63	1.43	1.26	1.11	0.973	0.855	0.752	0.661	
8.3	1.52	1.52	1.39	1.22	1.07	0.941	0.827	0.727	0.639	0.562	
8.4	1.29	1.29	1.17	1.03	0.906	0.796	0.700	0.615	0.541	0.475	
8.5	1.09	1.09	0.990	0.870	0.765	0.672	0.591	0.520	0.457	0.401	
8.6	0.920	0.920	0.836	0.735	0.646	0.568	0.499	0.439	0.386	0.339	
8.7	0.778	0.778	0.707	0.622	0.547	0.480	0.422	0.371	0.326	0.287	
8.8	0.661	0.661	0.601	0.528	0.464	0.408	0.359	0.315	0.277	0.244	
8.9	0.565	0.565	0.513	0.451	0.397	0.349	0.306	0.269	0.237	0.208	
9.0	0.486	0.486	0.442	0.389	0.342	0.300	0.264	0.232	0.204	0.179	

¹ The freshwater chronic water quality criteria for total ammonia when fish early life stages may be present were calculated using the following equation, which may also be used to calculate unlisted values:

Freshwater chronic water quality criterion for ammonia (fish early life stages present) =

$$\left[\begin{array}{c} \frac{0.0577}{(1+10^{7.688-pH})} + \frac{2.487}{(1+10^{pH-7.688})} \end{array}\right] \times \text{MIN} \left[2.85, 1.45 \times 10^{0.028 \times (25-T)}\right] \text{ where } T = {}^{\circ}\text{C}.$$

× Indicates multiplication. MIN indicates the lesser of the two values separated by a comma.

NOTES:

pH and temperature are field measurements taken at the same time and location as the water sample destined for the laboratory analysis of ammonia. If field measured pH and/or temperature values fall between the above tabular values, round field measured values according to standard rounding procedures to nearest tabular value to determine ammonia standard or use above described equation.

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Table 3. The thirty-day average (Chronic Criteria) concentration for Total Ammonia (in mg nitrogen per liter) for the protection of fresh water aquatic life when fish early life stages are absent. (The concentration of total ammonia may not exceed the chronic more than once every three years on the average. In addition, the highest 4-day average within the 30-day period should not exceed 2.5 times the chronic criterion.)

TABLE 3. CHRONIC AMMONIA CRITERIA FOR WATERS WHERE FRESHWATER FISH EARLY LIFE STAGES ARE ABSENT											
		WHER	E FRESHV				ES ARE A	BSENT			
(mg Nitrogen/L) ¹											
**	Temperature (°C)										
pН	0-7	8	9	10	11	12	13	14	15 ²	16 ²	
6.5	10.8	10.1	9.51	8.92	8.36	7.84	7.35	6.89	6.46	6.06	
6.6	10.7	9.99	9.37	8.79	8.24	7.72	7.24	6.79	6.36	5.97	
6.7	10.5	9.81	9.20	8.62	8.08	7.58	7.11	6.66	6.25	5.86	
6.8	10.2	9.58	8.98	8.42	7.90	7.40	6.94	6.51	6.10	5.72	
6.9	9.93	9.31	8.73	8.19	7.68	7.20	6.75	6.33	5.93	5.56	
7.0	9.60	9.00	8.43	7.91	7.41	6.95	6.52	6.11	5.73	5.37	
7.1	9.20	8.63	8.09	7.58	7.11	6.67	6.25	5.86	5.49	5.15	
7.2	8.75	8.20	7.69	7.21	6.76	6.34	5.94	5.57	5.22	4.90	
7.3	8.24	7.73	7.25	6.79	6.37	5.97	5.60	5.25	4.92	4.61	
7.4	7.69	7.21	6.76	6.33	5.94	5.57	5.22	4.89	4.59	4.30	
7.5	7.09	6.64	6.23	5.84	5.48	5.13	4.81	4.51	4.23	3.97	
7.6	6.46	6.05	5.67	5.32	4.99	4.68	4.38	4.11	3.85	3.61	
7.7	5.81	5.45	5.11	4.79	4.49	4.21	3.95	3.70	3.47	3.25	
7.8	5.17	4.84	4.54	4.26	3.99	3.74	3.51	3.29	3.09	2.89	
7.9	4.54	4.26	3.99	3.74	3.51	3.29	3.09	2.89	2.71	2.54	
8.0	3.95	3.70	3.47	3.26	3.05	2.86	2.68	2.52	2.36	2.21	
8.1	3.41	3.19	2.99	2.81	2.63	2.47	2.31	2.17	2.03	1.91	
8.2	2.91	2.73	2.56	2.40	2.25	2.11	1.98	1.85	1.74	1.63	
8.3	2.47	2.32	2.18	2.04	1.91	1.79	1.68	1.58	1.48	1.39	
8.4	2.09	1.96	1.84	1.73	1.62	1.52	1.42	1.33	1.25	1.17	
8.5	1.77	1.66	1.55	1.46	1.37	1.28	1.20	1.13	1.06	0.990	
8.6	1.49	1.40	1.31	1.23	1.15	1.08	1.01	0.951	0.892	0.836	
8.7	1.26	1.18	1.11	1.04	0.976	0.915	0.858	0.805	0.754	0.707	
8.8	1.07	1.01	0.944	0.885	0.829	0.778	0.729	0.684	0.641	0.601	
8.9	0.917	0.860	0.806	0.756	0.709	0.664	0.623	0.584	0.548	0.513	
9.0	0.790	0.740	0.694	0.651	0.610	0.572	0.536	0.503	0.471	0.442	

¹ The freshwater chronic water quality criteria for total ammonia where fish early life stages are absent were calculated using the following equation, which may also be used to calculate unlisted values:

Freshwater chronic water quality criterion for ammonia (fish early life stages absent) =

$$\left[\begin{array}{c} 0.0577 \\ (1+10^{7.688-pH}) \end{array} + \frac{2.487}{(1+10^{pH-7.688})} \right] \times 1.45 \times \left[10^{-0.028 \times (25-MAX(T,7))}\right] \text{ where T} = ^{\circ}\text{C}.$$

× Indicates multiplication. MAX indicates the greater of the two values separated by a comma.

NOTES:

pH and temperature are field measurements taken at the same time and location as the water sample destined for the laboratory analysis of ammonia. If field measured pH and/or temperature values fall between the above tabular values, round field measured values according to standard rounding procedures to nearest tabular value to determine ammonia standard or use above described equation.

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²At 15°C and above, the criterion for fish early life stages absent is the same as the criterion for fish early life stages present.

- early life stages absent), the chronic criteria are just pH dependent, and
- at a particular water temperature, the chronic criteria are more restrictive with increasing pH values, and at a constant pH value, criteria values decrease as a function of temperature.

Beneficial Uses

Ammonia water quality standards have been established in the Nevada water quality regulations for protection and propagation of aquatic life.

Existing Water Quality Standards for Ammonia

The existing aquatic life ammonia criteria contained in the water quality regulations are single-value numerical limits which are differentiated, for the most part, depending on whether the waterbody contains coldwater or warmwater fish. Generally, for waters with coldwater fish, a criteria of 0.02 mg/L unionized ammonia (NH₃) was established as recommended in EPA's <u>Quality Criteria for Water (1976)</u> and <u>Ambient Water Quality Criteria for Ammonia (1984)</u>. To protect warmwater fish, a single-value numerical water quality standard of 0.06 mg/L NH₃ was adopted as recommended in EPA's <u>Ambient Water Quality Criteria for Ammonia (1984)</u>.

Exceptions to the above generalizations include the lower Carson River (from New Empire to Lahontan Dam) and the Humboldt River, which contain warmwater fish but have a 0.02 mg/L NH₃ standard. Lake Mead including Inner Las Vegas Bay which is designated as a warmwater fishery has an unionized ammonia standard, expressed as N, of 0.45 mg/L (acute) and 0.05 mg/L (chronic) involving somewhat complicated calculations requiring averaging of samples at various depths while accounting for diurnal fluctuations. Lake Tahoe and its tributaries have single-value un-ionized ammonia standards of 0.003 mg/L and 0.004 mg/L, respectively.

Besides the aforementioned ammonia aquatic life criteria, NAC 445A.119, "Criteria of Water Quality

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for Designated Beneficial Uses" also contains a municipal or domestic supply beneficial use ammonia water quality limit. Because ammonia may be indicative of pollution and because of its significant effect on chlorination, it is recommended that total ammonia nitrogen in public water supply sources not exceed 0.5 mg/L (National Academy of Sciences, Water Qualtiy Criteria, Blue Book, 1972). This limit is only a guideline and is not a standard for any of the designated or class waterbodies contained in the water quality regulations.

Proposed Revision

Based on recommendations in the 1999 Ammonia Update, it is proposed to revise the following aspects of the existing water quality standards for ammonia:

- change ammonia aquatic life standards from single-value numerical limits to site-specific
 determinations, calculated via equations, depending on the presence or absence of
 sensitive cold water fish species, and if fish early life stages are expected to be present,
 and
- express the calculated ammonia criteria as total ammonia nitrogen rather than as unionized ammonia.

It is proposed to incorporate the equations as presented in the EPA 1999 Ammonia Update for calculating ammonia aquatic life water quality standards into the water quality standards for waters of Nevada. The water quality standards, which have an existing ammonia standard, would be revised to reflect the updated ammonia criteria. No revision is proposed of the municipal or domestic supply limit discussed above.

The existing ammonia criteria for Lake Tahoe and tributaries, Lake Mead, and Las Vegas Wash are not proposed to be revised at this time. NDEP is assisting the Lahontan Regional Water Quality Control Board (LRWQCB) with developing Lake Tahoe Total Maximum Daily Loads (TMDLs). Through the TMDL process, water quality standard changes may be identified. Following completion of the technical TMDLs in 2004, NDEP will consider reviewing Lake Tahoe water quality standards.

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The Lake Mead ammonia criteria that were adopted in 1994 were developed based on site-specific conditions through the water column and were intended to provide protection for fish spatially and temporally. Although there is no water quality standard for ammonia in the Upper and Lower Las Vegas Wash, a seasonal TMDL for point source discharges to the Wash was established in 1988. Revisions to the ammonia criteria and evaluation of impacts to existing TMDL requirements will be done as part of future site-specific water quality standards review for Lake Mead and Las Vegas Wash.

The Class Waters standards are currently being reviewed by NDEP. Changes to the ammonia criteria to reflect EPA's most recent recommendations will be made when the Class Waters standards are assessed as part of NDEP's triennial review schedule of established water quality standards.

At this time, Smoke, Bronco, and Gray Creeks (NAC 445A.180 to 445A.182) do not have ammonia standards, nor do they have beneficial uses defined in the regulations. Future reviews of these water bodies will address the addition of beneficial uses and incorporation of appropriate ammonia water quality standards.

Authorized tribes have independent authority for setting water quality standards and implementing regulations for waters on reservation lands under the 1987 Amendments to the Clean Water Act. At this time, the State of Nevada regulations include water quality standards for waterbodies on tribal lands throughout Nevada. However, the State of Nevada has no authority to set standards on tribal lands, therefore, the water quality standards contained in NAC 445A.168 (Walker River at Schurz Bridge), NAC 445A.190 (Truckee River at Pyramid Lake), and NAC 445A.224 (East Fork Owyhee River at the Nevada-Idaho stateline) are not proposed to be modified to include total ammonia aquatic life water quality criteria.

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Evaluation of Proposed Ammonia Water Quality Standards

To evaluate whether the new proposed ammonia aquatic life criteria will be more or less restrictive than the existing numeric ammonia standards, total ammonia acute and chronic criteria values were calculated using the 1999 Update equations and the pH and seasonal temperature values contained in the water quality standards specific to each river system and waterbody. Existing un-ionized ammonia standards contained in the water quality regulations were converted to total ammonia values for comparison. This comparison between the existing and the new proposed criteria values is shown in Table 4 (Table 4 included on pages 16 - 22 of this document).

Acute ammonia criteria were calculated based on the pH water quality standard and whether the waterbody contains coldwater or warmwater fish species. The pH and temperature dependent equation from the 1999 Update for when fish early life stages are expected to be present was used to calculate the chronic ammonia criteria values. Existing numerical un-ionized ammonia standards were converted to total ammonia values using the chemical equilibrium relationships presented in the Appendix. Conversions of un-ionized ammonia values to total ammonia values is a function of pH and temperature, and consequently, as shown in Table 4, the calculated total ammonia values vary depending on the waterbody's pH and seasonal temperature water quality standards. Example calculations of the conversion of un-ionized ammonia values to total ammonia values and the determination of the new proposed acute and chronic ammonia criteria are shown in the Appendix.

The evaluation of proposed and existing ammonia water quality standards (Table 4) has been done by river basin or system. The individual reaches of each river system having similar water quality pH ranges and seasonal temperature standards have been grouped together. The Humboldt River water quality regulations do not contain specific numerical temperature standards. To evaluate the proposed and the existing ammonia water quality standards for the Humboldt River, temperature ranges contained in the regulations for other waterbodies that contain warmwater fish species were used.

As shown in Table 4, the new proposed ammonia acute criteria vary depending on whether the waterbody contains coldwater or warmwater fish, and the pH of the waterbody. The acute criteria are constant as a function of the waterbody temperature. The new proposed chronic criteria for when fish early life stages are expected to be present vary as a function of pH and temperature.

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The overall generalizations that can be made from the comparisons, presented in Table 4, is the new proposed total ammonia acute criteria will usually be less restrictive than the existing ammonia water quality standards when expressed as total ammonia nitrogen. For a particular temperature, the proposed chronic criteria for when fish early life stages are expected to be present will be more restrictive than the existing criteria at the lower water quality pH standards (pH 6.5 or pH 7.0). At the higher water quality pH standards (pH 8.3 or pH 9.0), the proposed criteria will be less restrictive than the existing criteria for a particular temperature. As can be seen from the tabulated data in Table 4, on a seasonal basis, the proposed ammonia chronic criteria for the designated waterbodies will be more restrictive during the summer and early fall periods compared to the winter and spring months.

The current surface water monitoring program operated by NDEP involves collecting water quality samples from the major water systems of the State on a routine basis. These "grab samples" are used to evaluate the quality of the waters, to assess compliance with the water quality standards, and to determine whether the waterbodies are supportive of their intended uses.

In evaluating whether ammonia water quality standards are being attained, the grab samples collected from the surface waters monitoring network, which can be every two or three months depending on the waterbody, may not be representative of conditions over a 30-day period due to the variable characteristics of the waterbodies and constituents. Therefore, to assess whether the waterbody is in compliance with the ammonia aquatic life criteria, NDEP proposes to compare grab sample concentrations to the ammonia 1-hour aquatic life criteria (acute). Exceedance of the acute criteria, more than once over a 3-year period on the average, would indicate that a more intensive waterbody sampling program may need to be conducted over a 30-day period to evaluate whether ammonia concentrations are in exceedance of the applicable chronic aquatic life criteria.

The recently published 2002 303(d) Impaired Waters list for the State did not contain any waterbodies being listed for exceeding the existing un-ionized ammonia water quality standard. On prior 303(d) lists, no waterbodies have been listed as impaired for exceeding ammonia aquatic life standards. Since the new proposed total ammonia acute (1-hour average) aquatic life criteria will be less restrictive than the existing ammonia standards when expressed as total ammonia, as was illustrated in Table 4, it is not anticipated that the proposed revision of the ammonia aquatic life criteria will affect standards compliance.

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Summary of Proposed Regulatory Changes

The approach recommended by EPA in the 1999 Update document involves formulating revised acute (1 hour average) and chronic (30 day average) aquatic life water quality criteria for ammonia that account for the temperature- and pH-dependence of ammonia toxicity. Rather than adopt a single-value numeric standard, mathematical equations have been developed by EPA for determining ammonia acute criterion as a function of pH and whether sensitive coldwater fish species are present. Freshwater ammonia chronic criteria are calculated based on the pH and temperature of the waterbody and whether fish early life stages are expected to be present.

The water quality regulatory changes outlined in this proposal would involve removing the existing unionized ammonia single-value (S.V.) limit from the water quality standards for designated river systems and waterbodies. A total ammonia (as nitrogen) water quality standard for protection of aquatic life would be added as a new parameter in the water quality regulations.

The water quality regulations to be amended are summarized below:

NAC 445A.147 to 445A.158	Carson River System
NAC 445A.160 to 445A.169	Walker River System East Walker River at Bridge B-1475 (new regulation) Walker Lake (new regulation)
NAC 445A.171 to 445A.173	Interstate Waters
NAC 445A.175 to 445A.179	Virgin River System
NAC 445A.184 to 445A.190	Truckee River System
NAC 445A.192 to 445A.193	Colorado River System
NAC 445A.203 to 445A.208	Humboldt River System
NAC 445A.210 to 445A.212	Muddy River System

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NAC 445A.215 to 445A.225 Snake River System

No regulation changes are proposed for the following:

NAC 445A.123 – 127	Class	Waters

NAC 445A.180 Smoke Creek

NAC 445A.181 Bronco Creek

NAC 445A.182 Gray Creek

NAC 445A.191 Lake Tahoe

NAC 445A.1915 Lake Tahoe Tributaries

NAC 445A.195 & 197 Lake Mead and Inner Las Vegas Bay

NAC 445A.199 & 201 Upper and Lower Las Vegas Wash

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Carson River System

West Fork at Stateline (NAC 445A.147) Bryant Creek at Stateline (NAC 445A.148) East Fork at Stateline (NAC 445A.149) East Fork at Riverview (NAC 445A.150) East Fork at Muller Lane (NAC 445A.151)

Existing Ammonia std: 0.02 mg/L NH₃

		Prop	osed Total A	Ammonia C mg/L)		mmonia (as N, Existing Standard	
Wtr Temp (°	C)	рŀ	H 6.5	pН	pH 6.5	pH 9.0	
	•	Acute ¹	Chronic ²	Acute ¹	Chronic ²	-	-
Nov – May	Nov – May		6.67	0.885	0.486	22.2	0.087
13							
June	17	32.6	5.66	0.885	0.413	16.4	0.068
July	21	32.6	4.37	0.885 0.319		12.2	0.055
Aug - Oct	22	32.6	4.12	0.885	0.300	11.4	0.052

¹ Acute criteria for coldwater fish present

Carson River at Genoa Lane (NAC 445A.152) Carson River at Cradlebaugh Bridge (NAC 445A.153) Carson River at Mexican Ditch Gage (NAC 445A.154)

Existing Ammonia std: 0.02 mg/L NH₃

		Propo	sed Total A	Ammonia (Calc. Total Ammo	onia (as N, mg/L)	
		1		mg/L)		based on Exis	
Wtr Temp (°	Wtr Temp (°C) pH 6.5 pH			I 9.0	pH 6.5	pH 9.0	
		Acute ¹	Chronic ²	Acute ¹	Chronic ²		
Nov - Apr	13	32.6	6.67	0.885	0.486	22.2	0.087
May - June	17	32.6	5.66	0.885	0.413	16.4	0.068
July - Oct	23	32.6	3.85	0.885	0.280	10.6	0.050

¹ Acute criteria for coldwater fish present

Carson River at New Empire (NAC 445A.155)

Existing Ammonia std: 0.02 mg/L NH₃

	Propo	osed Total A			onia (as N, mg/L)	
		(as N,	mg/L)		based on Exis	sting Standard
Wtr Temp (°C)	pН	I 6.5	pН	9.0	pH 6.5	pH 9.0
	Acute ¹	Chronic ²	Acute ¹	Chronic ²		
Nov - May 18	32.6	5.33	0.885	0.387	15.2	0.065
June - Oct 32.6		3.85	0.885	0.280	10.6	0.050
23						

¹ Acute criteria for coldwater fish present

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² Chronic criteria for fish early life stages present

² Chronic criteria for fish early life stages present

² Chronic criteria for fish early life stages present

Carson River at Dayton Bridge (445A.156) Carson River at Weeks (NAC 445A.157)

Existing Ammonia std: 0.02 mg/L NH₃

		Propo	osed Total A (as N,	mmonia (mg/L)		onia (as N, mg/L) sting Standard	
Wtr Temp (°	°C)	pН	pH 6.5		I 9.0	pH 6.5	pH 9.0
	Ac		Chronic ²	Acute ¹	Chronic ²		
Nov - Mar	11	32.6	6.67	0.885	0.486	25.9	0.098
Apr - June	24	32.6	3.62	0.885	0.264	9.9	0.048
July - Oct	28	32.6	2.80	0.885	0.204	7.4	0.040

Carson River at Lahontan Dam (NAC 445A.158)

Existing Ammonia std: 0.02 mg/L NH₃

		Propo	sed Total A	Ammonia (Calc. Tot. Ammo		
			(as N,	mg/L)		based on Exis	sting Standard
Wtr Temp (°	C)	pH 7.0		pН	1 8.3	pH 7.0	pH 8.3
		Acute ¹	Chronic ²	Acute ¹	Chronic ²		
Nov - Mar	11	36.1	5.91	4.71	1.52	25.9	0.098
Apr - June	24	36.1	3.21	4.71	0.827	9.9	0.048
July - Oct	28	36.1	2.48	4.71	0.639	7.4	0.040

¹ Acute criteria for warmwater fish present

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Acute criteria for coldwater fish present

Chronic criteria for fish early life stages present

² Chronic criteria for fish early life stages present

Walker River System

West Walker at Stateline (NAC 445A.160)

Topaz Lane (NAC 445A.161)

West Walker near Wellington (NAC 445A.162)

West Walker above confluence with East Walker (NAC 445A.163)

Sweetwater Creek (NAC 445A.164)

Existing Ammonia std: 0.02 mg/L NH₃

East Walker at Stateline (NAC 445A.165)

East Walker south of Yerington (NAC 445A.166)

Desert Creek (NAC 445A.169)

		Propo	sed Total A	Ammonia (Calc. Tot. Ammo	` ' ' '	
			(as N,	mg/L)	based on Exis	sting Standard	
Wtr Temp (°	C)	pН	I 6.5	pН	9.0	pH 6.5	pH 9.0
	Acute ¹ Chronic ² Acute ¹ Chronic ²						
Nov – Apr	13	32.6	6.67	0.885	0.486	22.2	0.087
May - June	17	32.6	5.66	0.885	0.413	16.4	0.068
Jul - Oct	23	32.6	3.85	0.885 0.280		10.6	0.050

Acute criteria for coldwater fish present

Walker River at Inlet Weber Reservoir (NAC 445A.167)

Existing Ammonia std: 0.06 mg/L NH₃

		Propo	sed Total A	Ammonia (Calc. Tot. Ammonia (as N, mg/L)			
			(as N,	mg/L)		based on Existing Standard		
Wtr Temp (°	(C)	pН	I 6.5	pН	9.0	pH 6.5	pH 9.0	
		Acute ¹	Chronic ²	Acute ¹	Chronic ²			
Nov - Mar 13		48.8	6.67	1.32	0.486	66.5	0.259	
Apr - June 24		48.8	3.62	1.32	0.264	29.5	0.143	
July - Oct	aly - Oct 28 48.8 2.80			1.32	0.204	22.3	0.120	

¹ Acute criteria for warmwater fish present

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² Chronic criteria for fish early life stages present

² Chronic criteria for fish early life stages present

Interstate Waters

Chiatovich Creek (NAC 445A.171) Indian Creek (NAC 445A.172) Leidy Creek (NAC 445A.173)

Existing Ammonia std: 0.02 mg/L NH₃

		Propo	osed Total A (as N,	mmonia (mg/L)	Calc. Tot. Ammonia (as N, mg/L) based on Existing Standard		
Wtr Temp (°	C)	pН	17.0	pН	I 8.3	pH 7.0	pH 8.3
		Acute ¹	Chronic ²	Acute ¹	Chronic ²		
Nov - Apr 13		24.1	5.91	3.15	1.52	7.03	0.368
May - June 17		24.1	5.02	3.15	1.29	5.20	0.276
July - Oct			3.36	0.184			

Acute criteria for coldwater fish present

Virgin River System

Virgin River at Mesquite (NAC 445A.175) Virgin River at Stateline (Littlefield) (NAC 445A.176) Virgin River at Riverside (NAC 445A.177) Existing Ammonia std: 0.06 mg/L NH₃

		Propo	sed Total A	mmonia (Calc. Tot. Ammonia (as N, mg/L)			
			(as N,	mg/L)		based on Existing Standard		
Wtr Temp (°C)		pН	H 7.0 pH		[9.0	pH 7.0	pH 9.0	
		Acute ¹	Chronic ²	Acute ¹	Chronic ²			
Nov - June 21		36.1	3.88	1.32	0.319	11.6	0.165	
July - Oct 32		36.1	1.91	1.32	0.157	5.40	0.103	

Acute criteria for warmwater fish present

Beaver Dam Wash (445A.178) Snake Creek (NAC 445A.179)

Existing Ammonia std: 0.02 mg/L NH₃

	Propo	sed Total A	Ammonia (Calc. Tot. Ammonia (as N, mg/L)			
		(as N,	mg/L)		based on Existing Standard		
Wtr Temp (°C)	pН	17.0	pН	I 8.3	pH 7.0	pH 8.3	
	Acute ¹	Chronic ²	Acute ¹	Chronic ²			
Nov - Apr 13	24.1	5.91	3.15	1.52	7.03	0.368	
May - June 17	24.1	5.02	3.15	1.29	5.20	0.276	
July - Oct 23 24.1 3.41			3.15	0.88	3.36	0.184	

¹ Acute criteria for coldwater fish present

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² Chronic criteria for fish early life stages present

² Chronic criteria for fish early life stages present

² Chronic criteria for fish early life stages present

Truckee River System

Truckee River at Stateline (NAC 445A.184)
Truckee River at Idlewild (NAC 445A.185)
Truckee River at East McCarran (NAC 445A.186)

Existing Ammonia std: 0.02 mg/L NH₃

		Propo	sed Total A	Ammonia (Calc. Tot. Ammonia (as N, mg/L)			
			(as N,	mg/L)		based on Existing Standard		
Wtr Temp (°	C)	pН	I 6.5	pН	0.0	pH 6.5	pH 9.0	
		Acute ¹	Chronic ²	Acute ¹	Chronic ²			
Nov - Mar	7	32.6	6.67	0.885	0.486	35.5	0.129	
Apr – May	13	32.6	6.67	0.885	0.486	22.2	0.087	
June	17	32.6	5.66	0.885	0.413	16.4	0.068	
July	21	32.6 4.37		0.885	0.319	12.2	0.055	
August	22	32.6 4.12 0.885 0.299				11.4	0.052	
Sep - Oct	23	32.6	3.85	0.885	0.280	10.6	0.050	

¹ Acute criteria for coldwater fish present

Truckee River at Lockwood Bridge (NAC 445A.187) Truckee River at Derby Dam (NAC 445A.188)

Existing Ammonia std: 0.02 mg/L NH₃

		Propo	osed Total A (as N,	mmonia (mg/L)	Calc. Tot. Ammonia (as N, mg/L) based on Existing Standard		
Wtr Temp (°	C)	pН	I 6.5	рН	9.0	pH 6.5	pH 9.0
•		Acute ¹	Chronic ²	Acute ¹	Chronic ²		
Nov – Mar	13	32.6	6.67	0.885	0.486	22.2	0.087
April	21	32.6	4.37	0.885	0.319	12.2	0.055
May	22	32.6 4.12 0.885 0.29				11.4	0.052
June - Oct	23	32.6	3.85	0.885	0.280	10.6	0.050

¹ Acute criteria for coldwater fish present

Truckee River at Wadsworth Gage (NAC 445A.189)

Existing Ammonia std: 0.02 mg/L NH₃

		Propo	sed Total A	Ammonia (Calc. Tot. Ammonia (as N, mg/L)			
			(as N,	mg/L)		based on Existing Standard		
Wtr Temp (°C	C)	pН	[6.5	рН	9.0	pH 6.5	pH 9.0	
		Acute ¹	Chronic ²	Acute ¹	Chronic ²			
Nov – Mar 13		32.6	6.67	0.885	0.486	22.2	0.087	
Apr - June 14		32.6	6.67	0.885	0.486	20.6	0.082	
July - Oct 25 32.6 3.38			0.885	0.247	9.2	0.045		

¹ Acute criteria for coldwater fish present

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² Chronic criteria for fish early life stages present

² Chronic criteria for fish early life stages present

² Chronic criteria for fish early life stages present

Colorado River System

Colorado River below Davis Dam (NAC 445A.192) Colorado River below Hoover Dam (NAC 445A.193) Existing Ammonia std: 0.02 mg/L NH₃

		Propo	sed Total A	mmonia (Calc. Tot. Ammonia (as N, mg/L)			
			(as N,	mg/L)		based on Existing Standard		
Wtr Temp (°0	C)	pH 7.0 pH 8.3				pH 7.0	pH 8.3	
	Acute ¹ Chronic ² Acute ¹ Chronic ²							
Nov – Mar	Nov – Mar 13 24.1 5.91 3		3.15	1.52	7.03	0.368		
Apr - June 17 24.1 5.02		3.15	1.29	5.20	0.276			
July - Oct	23	24.1	3.41	3.15	0.88	3.36	0.184	

Acute criteria for coldwater fish present

Muddy River System

Muddy River at Glendale Bridge (NAC 445A.210) Muddy River at Overton (NAC 445A.211) Meadow Valley Wash (NAC 445A.212) Existing Ammonia std: 0.06 mg/L NH₃

		Propo	sed Total A	Ammonia (Calc. Tot. Ammonia (as N, mg/L)			
			(as N,	mg/L)		based on Existing Standard		
Wtr Temp (°	C)	pН	H 7.0 pH		1 9.0	pH 7.0	pH 9.0	
		Acute ¹	Chronic ²	Acute ¹	Chronic ²			
Nov - June 21		36.1	3.88	1.32	0.319	11.6	0.165	
July – Oct 32 36.1 1.91			1.32	0.157	5.4	0.103		

Acute criteria for warmwater fish present

Humboldt River System

Humboldt River near Osino (NAC 445A.203) Humboldt River at Palisade Gage (NAC 445A.204) Humboldt River at Battle Mountain Gage (NAC 445A.205) Humboldt River at crossing of state highway 789 (NAC 445A.206) Humboldt River at Imlay (NAC 445A.207) Humboldt River at Woolsey (NAC 445A.208) Existing Ammonia std: 0.02 mg/L NH₃

		Propo	osed Total A (as N,	Ammonia (mg/L)		onia (as N, mg/L) sting Standard	
Wtr Temp (°C) pH 6.5			I 6.5	pН	I 9.0	pH 6.5	pH 9.0
		Acute ¹	Chronic ²	Acute ¹	Chronic ²		
Nov – Mar	11	48.8	6.67	1.32	0.486	25.9	0.098
Apr - June 24		48.8	3.62	1.32	0.263	9.9	0.048
July - Oct	28				0.203	7.4	0.040

¹ Acute criteria for warmwater fish present

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² Chronic criteria for fish early life stages present

² Chronic criteria for fish early life stages present

² Chronic criteria for fish early life stages present

Snake River System

Big Goose Creek (NAC 445A.215) Salmon Falls Creek (NAC 445A.216) Shoshone Creek (NAC 445A.217) Owyhee River, South Fork (NAC 445A.225)

Existing Ammonia std: 0.02 mg/L NH₃

		Propo	sed Total A		Calc. Tot. Ammonia (as N, mg/L)			
			(as N,	mg/L)		based on Existing Standard		
Wtr Temp (°	C)	pН	I 6.5	6.5 pH 9.0		pH 6.5	pH 9.0	
		Acute ¹	Chronic ²	Acute ¹	Chronic ²			
Nov – Apr	13	32.6	6.67	0.885	0.486	22.2	0.087	
May - Oct	21	32.6	4.37	0.885	0.319	12.2	0.055	

¹ Acute criteria for coldwater fish present

Jarbidge River: East Fork (NAC 445A.218)

Jarbidge River upstream from Jarbidge (NAC 445A.219) Jarbidge River downstream from Jarbidge (NAC 445A.220)

Bruneau River: West Fork (NAC 445A.221) Existing Ammonia std:
Owyhee River: East Fork above Mill Creek (NAC 445A.222) 0.02 mg/L NH₃

Owyhee River: East Fork south of Owyhee (NAC 445A.223)

		Propo	sed Total A		Calc. Tot. Ammonia (as N, mg/L)			
			(as N,	mg/L)		based on Existing Standard		
Wtr Temp (°	C)	pН	I 6.5	pН	1 9.0	pH 6.5	pH 9.0	
		Acute ¹	Chronic ²	Acute ¹	Chronic ²			
Nov – Apr 7		32.6	6.67	0.885	0.486	35.5	0.129	
May - Oct 21		32.6	4.37	0.885	0.319	12.2	0.055	

Acute criteria for coldwater fish present

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² Chronic criteria for fish early life stages present

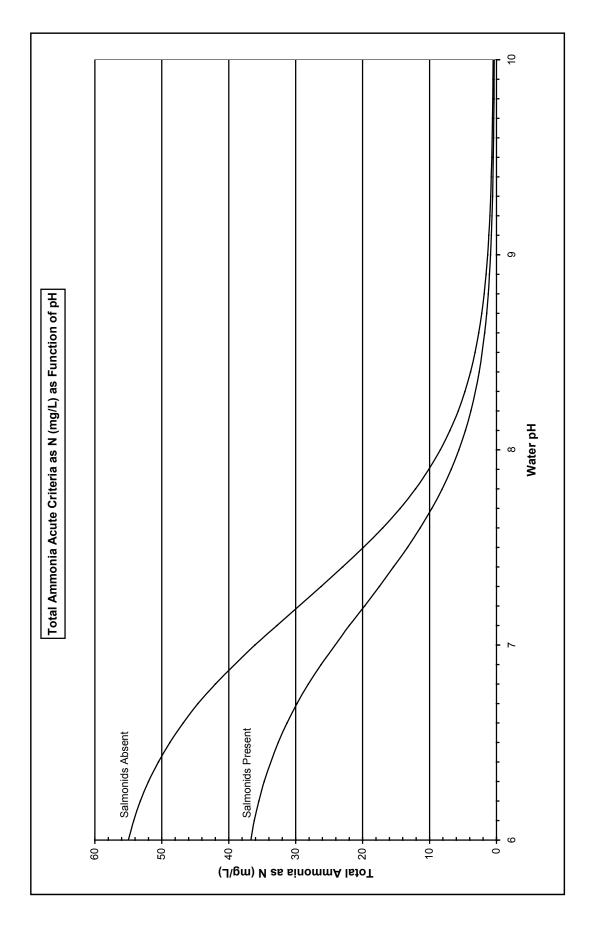
² Chronic criteria for fish early life stages present

FIGURES

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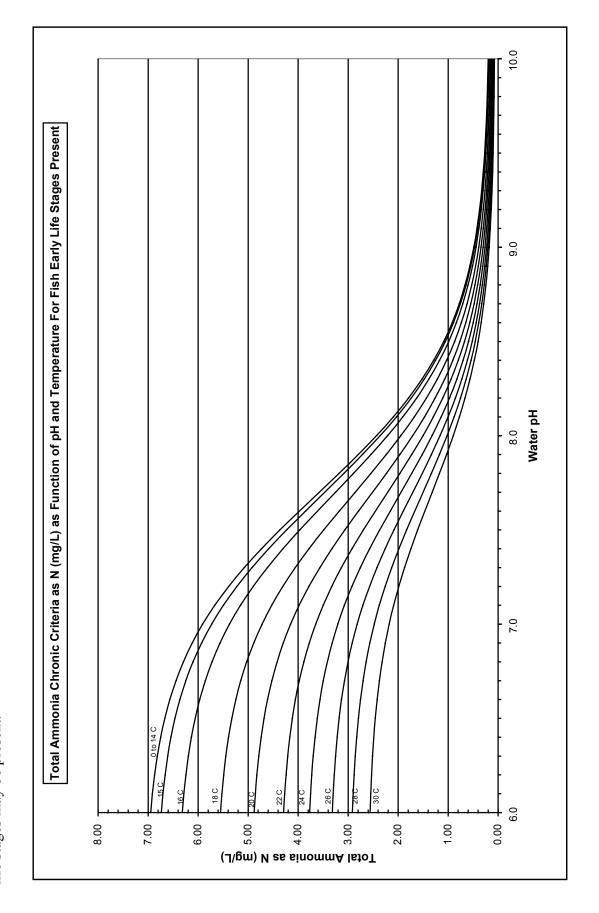
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Figure 1. The one-hour average (Acute Criteria) concentration for Total Ammonia (in mg nitrogen per liter) as function of pH.



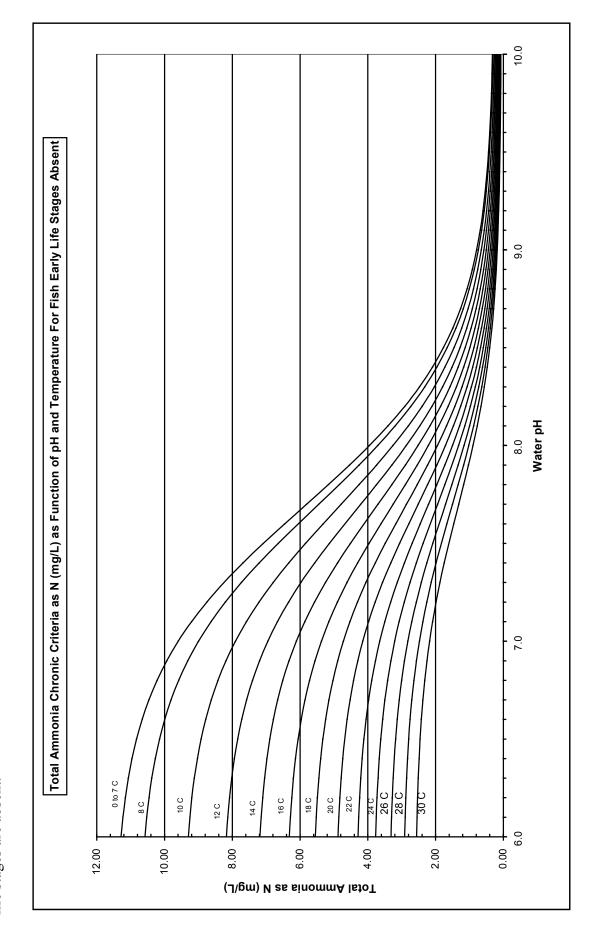
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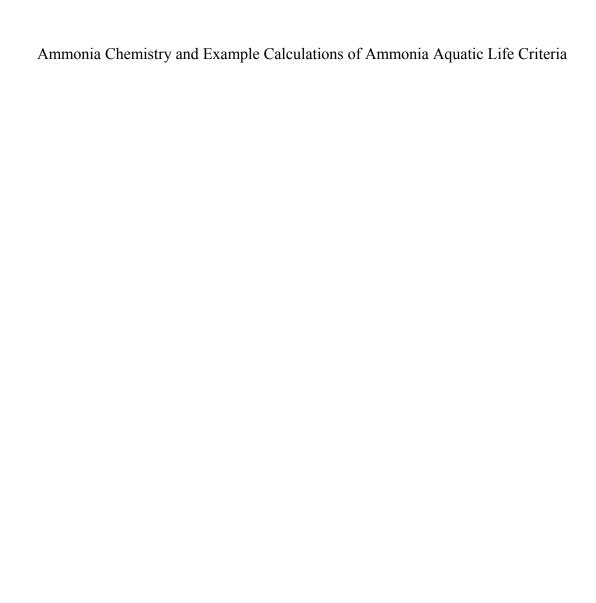
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APPENDIX



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Appendix: Ammonia Chemistry and Example Calculations of Ammonia Aquatic Life Criteria

The term total ammonia refers to the sum of the two ammonia species NH₃ (un-ionized ammonia) and NH₄⁺ (ammonium) and can be represented mathematically as:

$$[Total Ammonia] = [NH3] + [NH4+]$$
 (1)

where [] denotes concentrations.

In solutions, the two forms of ammonia exist in chemical equilibrium with one another and a simplified chemical equation can be written to describe this relationship:

$$NH_4^+ \leftrightarrow NH_3 + H^+$$
 (2)

The ratio of the products to reactants for the above reaction can be expressed by the following relationship:

$$K = \frac{\left[NH_3\right]\left[H^+\right]}{\left[NH_4^+\right]} \tag{3}$$

where K is referred to as the equilibrium constant.

At a temperature of 25 °C and a solution pH of 9.24, the concentrations of NH₃ and NH₄⁺ in solution will be equal. At a higher solution pH and/or temperature, the equilibrium of the above chemical reaction (2) will shift to the right resulting in more ammonia being present in the un-ionized form (NH₃). The chemical equilibrium of the above reaction will shift to the left at lower pH and/or temperatures resulting in the ammonium ion being the predominant ammonia form present in the water.

Mathematical expressions can be developed to illustrate the relationships between pH and temperature and the aqueous ammonia species present in solution using the aforementioned relationships, and the following chemistry relationships.

$$pK = -\log_{10}[K] \tag{4}$$

$$pH = -log_{10}[H^{+}]$$
 (5)

By taking the antilogarithm of the above expressions, (4) and (5) can be rewritten as:

$$10^{pK} = -(K) \text{ or } K = 10^{-pK}$$
 (4)

$$10^{pH} = -(H^{+}) \text{ or } H^{+} = 10^{-pH}$$
 (5)

The equilibrium equation (3) can be rearranged as:

$$\frac{K}{\left[H^{+}\right]} = \frac{\left[NH_{3}\right]}{\left[NH_{4}^{+}\right]}$$

and rewritten as:

$$10^{pH-pK} = \frac{[NH_3]}{[NH_4^+]} \qquad \text{where } \frac{K}{[H^+]} = \frac{10^{-pK}}{10^{-pH}} = 10^{pH-pK}$$
 (6)

using relationships (4) and (5).

By substitution and rearrangement of terms, equation (1) can be rewritten as:

[Total Ammonia] =
$$\frac{\left[NH_3\right]\left[10^{\text{pH-pK}} + 1\right]}{\left[10^{\text{pH-pK}}\right]}$$
(7)

which can be rearranged to:

$$[NH_3] = \frac{[Total Ammonia][10^{pH-pK}]}{[10^{pH-pK} + 1]}$$
(8)

The expression for [NH₄⁺] which is shown below can be derived through a similar process:

$$[NH_4^+] = \frac{[TotalAmmonia]}{10^{pH-pK} + 1}$$
(9)

In equations (8) and (9), the constant pK is referred to as the dissociation constant for ammonia and is dependent on temperature according to the following equation which is specific to the dissociation of ammonia:

$$pK = 0.09018 + \frac{2729.92}{273.2 + T}$$
 (10)

where T = Degrees Celcius (° C).

The existing numerical un-ionized ammonia standards for the segments/reaches of the different river systems listed in Table 4 were converted to total ammonia values using the water quality beneficial use pH and seasonal temperature standards and the following chemical equilibrium relationships.

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$$[Total\ Ammonia] = \frac{\left[Un\ \text{-ionized}\ Ammonia\ as\ mg/L\ N\right]\!\!\left[\!10^{pH\ -pK}\ +1\right]}{\left[10^{pH\ -pK}\ \right]}$$

where [Un-ionized Ammonia as mg/L N] = [Un-ionized Ammonia as mg/L NH₃] \times 0.824

and pK =
$$0.09018 + \frac{2729.92}{273.2 + T}$$
 where T = ° C.

The calculations of total ammonia acute and chronic criteria using the 1999 Update equations are shown below. Conversion of un-ionized ammonia values to total ammonia values is also explained.

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Example Calculations using the 1999 Ammonia Update Equations:

Calculation of Total Ammonia Acute Criteria

For Coldwater Fish Species CMC =
$$\frac{0.275}{(1+10^{7.204-pH})} + \frac{39.0}{(1+10^{pH-7.204})}$$

At a solution pH of 7.5:
$$CMC = \frac{0.275}{(1+10^{7.204-7.5})} + \frac{39.0}{(1+10^{7.5-7.204})}$$

$$CMC = \frac{0.275}{(1+10^{-0.296})} + \frac{39.0}{(1+10^{0.296})} = \frac{0.275}{1.506} + \frac{39.0}{2.977} = 0.2 + 13.1 = \boxed{13.3}$$

For Warmwater Fish Species
$$CMC = \frac{0.411}{(1+10^{7.204-pH})} + \frac{58.4}{(1+10^{pH-7.204})}$$

At a solution pH of 7.5:
$$CMC = \frac{0.411}{(1+10^{7.204-7.5})} + \frac{58.4}{(1+10^{7.5-7.204})}$$

$$CMC = \frac{0.411}{(1+10^{-0.296})} + \frac{58.4}{(1+10^{0.296})} = \frac{0.411}{1.506} + \frac{58.4}{2.977} = 0.3 + 19.6 = \boxed{19.9}$$

The Total Ammonia Acute Criteria (1999 Update) are dependent only on pH. The equations do not contain a temperature variable. Instead, separate equations are applied depending on whether coldwater or warmwater fish species are present.

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Calculation of Total Ammonia Chronic Criteria

For Fish Early Life Stages Present

$$CCC = \left[\frac{0.0577}{(1+10^{7.688-pH})} + \frac{2.487}{(1+10^{pH-7.688})}\right] \times MIN \left[2.85, 1.45 \times 10^{0.028 \times (25-T)}\right]$$

At a solution pH of 7.5 and a temperature of 24 °C:

$$CCC = \left[\frac{0.0577}{(1+10^{7.688-7.5})} + \frac{2.487}{(1+10^{7.5-7.688})}\right] \times MIN [2.85, 1.45 \times 10^{0.028 \times (25-24)}]$$

$$CCC = \left[\frac{0.0577}{(1+10^{0.188})} + \frac{2.487}{(1+10^{-0.188})}\right] \times MIN [2.85, 1.45 \times 10^{0.028 \times (1)}]$$

$$CCC = \left[\frac{0.0577}{(1+1.542)} + \frac{2.487}{(1+0.649)}\right] \times MIN [2.85, 1.45 \times 1.067]$$

$$CCC = \left[\frac{0.0577}{(2.542)} + \frac{2.487}{(1.649)}\right] \times MIN [2.85, 1.547]$$

The temperature dependency of the chronic criteria (for fish early life stages present) is accounted for by the "MIN" relationship in the above equations. Interpretation of this empirical relationship is as follows:

MIN
$$[x, y]$$

If $x>y$ then MIN $[x, y] = y$
If $x then MIN $[x, y] = x$$

Therefore, in the above equation: MIN [2.85, 1.547] = 1.547

$$CCC = \left[\frac{0.0577}{(2.542)} + \frac{2.487}{(1.649)}\right] \times (1.547) = (0.023 + 1.508) \times (1.547) = (1.53) \times (1.547) = \boxed{2.37}$$

If the water body temperature was $14 \,^{\circ}$ C in the above example (pH = 7.5), the "MIN" relationship in the equation would be MIN [2.85, 2.947], which would be equal to 2.85, and the CCC equation would be:

 $CCC = (1.53) \times (2.85) = 4.36$

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Calculation of Total Ammonia Chronic Criteria

For Fish Early Life Stages Not Present

$$CCC = \left[\frac{0.0577}{(1+10^{7.688-pH})} + \frac{2.487}{(1+10^{pH-7.688})}\right] \times 1.45 \times \left[10^{0.028 \times (25-MAX(T,7))}\right]$$

At a solution pH of 7.5 and a temperature of 22 °C:

$$CCC = \left[\frac{0.0577}{(1+10^{7.688-7.5})} + \frac{2.487}{(1+10^{7.5-7.688})}\right] \times 1.45 \times \left[10^{0.028 \times (25-MAX(22,7))}\right]$$

The temperature dependency of the chronic criteria (for fish early life stages not present) is accounted for by the "MAX" relationship in the above equations. Interpretation of this empirical relationship is as follows:

MAX
$$[x, y]$$

If $x>y$ then MAX $[x, y] = x$
If $x then MAX $[x, y] = y$$

Therefore, in the above equation: MAX(22, 7) = 22

$$CCC = \left[\frac{0.0577}{(1+10^{0.188})} + \frac{2.487}{(1+10^{-0.188})}\right] \times 1.45 \times \left[10^{0.028 \times (25-22)}\right]$$

$$CCC = \left[\frac{0.0577}{(1+1.542)} + \frac{2.487}{(1+0.649)}\right] \times 1.45 \times \left[10^{0.028 \times (3)}\right]$$

$$CCC = \left[\frac{0.0577}{(2.542)} + \frac{2.487}{(1.649)}\right] \times 1.45 \times (10^{0.084})$$

$$CCC = (0.023 + 1.508) \times (1.45) \times (1.213) = (1.53) \times (1.45) \times (1.213) = \boxed{2.69}$$

If the water body temperature was $4 \,^{\circ}$ C in the above example (pH = 7.5), the "MAX" relationship in the equation would be MAX [4, 7], which would be equal to 7, and the CCC equation would be:

$$CCC = \left[\frac{0.0577}{(1+10^{0.188})} + \frac{2.487}{(1+10^{-0.188})}\right] \times 1.45 \times \left[10^{0.028 \times (25-7)}\right]$$

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For Fish Early Life Stages Not Present

$$CCC = \left[\frac{0.0577}{(1+1.542)} + \frac{2.487}{(1+0.649)}\right] \times 1.45 \times \left[10^{0.028 \times (18)}\right]$$

$$CCC = \left[\frac{0.0577}{(2.542)} + \frac{2.487}{(1.649)}\right] \times 1.45 \times (10^{0.504})$$

$$CCC = (0.023 + 1.508) \times (1.45) \times (3.2) = (1.53) \times (1.45) \times (3.2) = \boxed{7.09}$$

Conversion of Un-ionized Ammonia Values to Total Ammonia Values

The following equation can be derived from the ammonia chemical equilibrium relationships which were discussed above in detail.

[Total Ammonia] =
$$\frac{[NH_3][10^{pH-pK} + 1]}{[10^{pH-pK}]}$$
 (1)

The constant pK, referred to as the dissociation constant for ammonia, is dependent on temperature according to the following equation which is specific to the dissociation of ammonia:

pK =
$$0.09018 + \frac{2729.92}{273.2 + T}$$
 where T = ° C (2)

Example Conversion Calculation:

$$[NH_3] = 0.02 \text{ mg/L as NH}_3$$
 $T = 17 \,^{\circ} \text{ C}$ and $pH = 6.5$

Since it is desired to determine the Total Ammonia concentration as mg N/L, the un-ionized ammonia concentration must be expressed as mg N/L. This is accomplished by using chemical molecular weights and molar ratio conversions as explained and shown below:

molecular weight of $NH_3 = 17$ g/mole molecular weight of N = 14 g/mole

1 mole of NH₃ contains 1 mole of N

To convert X mg/L un-ionized ammonia as NH₃ to X mg/L un-ionized ammonia as N, need to determine the conversion factor which is derived below:

$$X \text{ mg/L NH}_3 \times \frac{1 moleNH_3}{17 gNH_3} \times \frac{1 moleN}{1 moleNH_3} \times \frac{14 gN}{1 moleN} = 0.824 \text{ (X)}$$
 so

[Un-ionized Ammonia as mg N/L] = [Un-ionized Ammonia as mg NH₃/L] \times 0.824

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Therefore, 0.02 mg/L un-ionized ammonia as $NH_3 = 0.0165 \text{ mg/L}$ un-ionized ammonia as N

At a T = 17 ° C
$$pK = 0.09018 + \frac{2729.92}{273.2 + 17} = 0.09018 + 9.407 = 9.4972096$$

By substituting these values and pH=6.5 into equation (1) from above:

[Total Ammonia] =
$$\frac{[NH_3][10^{pH-pK} + 1]}{[10^{pH-pK}]}$$

[Total Ammonia] =
$$\frac{\left[0.0165 \frac{mgN}{L}\right] \left[10^{6.5-9.4972096} + 1\right]}{\left[10^{6.5-9.4972096}\right]} = \frac{\left(0.0165\right) \left(10^{-2.9972096} + 1\right)}{10^{-2.9972096}}$$

[Total Ammonia] = 16.4 mg N/L

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